

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 316 588 A2**

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
04.06.2003 Bulletin 2003/23

(51) Int Cl.7: **C09B 67/22**, **C09B 29/33**,  
**C09D 11/02**

(21) Application number: **02258353.8**

(22) Date of filing: **03.12.2002**

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR**  
**IE IT LI LU MC NL PT SE SI SK TR**  
Designated Extension States:  
**AL LT LV MK RO**

(30) Priority: **03.12.2001 JP 2001368034**  
**03.12.2001 JP 2001368035**

(71) Applicant: **TOYO INK MANUFACTURING CO., LTD.**  
**Tokyo (JP)**

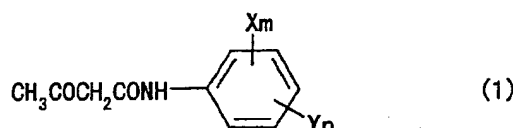
(72) Inventors:  
• **Ishigama, Takayoshi**  
**Chuo-ku, Tokyo 104-0031 (JP)**

• **Oshiba, Toshio**  
**Chuo-ku, Tokyo 104-0031 (JP)**  
• **Kawashima, Yoshinori**  
**Chuo-ku, Tokyo 104-0031 (JP)**  
• **Shiromaru, Osamu**  
**Chuo-ku, Tokyo 104-0031 (JP)**

(74) Representative: **Woods, Geoffrey Corlett**  
**J.A. KEMP & CO.**  
**Gray's Inn**  
**14 South Square**  
**London WC1R 5JJ (GB)**

(54) **Pigment yellow 74 and printing ink composition**

(57) A pigment yellow 74 obtainable by coupling a coupler component comprising 2-methoxyacetoacetoanilide and an acetoacetoanilide derivative of formula (1):



wherein each X may be the same or different and is  $\text{CONR}_1\text{R}_2$ ,  $\text{SO}_2\text{NR}_1\text{R}_2$ ,  $\text{NHCOR}_1$ ,  $\text{CONH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$  or  $\text{SO}_2\text{NH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$  (in which each of  $\text{R}_1$  and  $\text{R}_2$  is independently a hydrogen atom or an alkyl group, or  $\text{R}_1$  and  $\text{R}_2$  together form a cyclic structure, and  $k$  is an integer of 1 to 4),  $m$  is 1 or 2, each Y may be the same or different and is  $\text{R}_3$ ,  $\text{OR}_3$  (in which  $\text{R}_3$  is a hydrogen atom or an alkyl group),  $\text{COOH}$  or  $\text{SO}_3\text{H}$ , and  $n$  is an integer of 0 to 2, in an amount of 0.1 to 10 mol %, based on the 2-methoxyacetoacetoanilide, and a diazo component obtainable by diazotizing 2-methoxy-4-nitroaniline; and a printing ink composition comprising the above pigment yellow 74.

EP 1 316 588 A2

## Description

## Field of the Invention

- 5 [0001] The present invention relates to a pigment yellow 74 and a printing ink composition using it. More specifically, it relates to a pigment yellow 74 improved in color strength and transparency and a printing ink composition using it.

## Background of the Invention

- 10 [0002] Conventionally, as a yellow pigment for a printing ink, there has been used a disazo yellow pigment using 3,3'-dichlorobenzidine as a tetrazo component and an acetoacetoanilide compound as a coupling component. However, since the disazo yellow pigment has a biphenyl skeleton in its structure and contains chlorine, there is an apprehension of the generation of a toxic material at the time of disposing of a printed matter.

- 15 [0003] For this reason, it is strongly required to develop a yellow pigment which has pigment performance equivalent to that of the disazo yellow pigment and is producible at a low production cost and excellent in hygiene. Pigment yellow 74 using 2-methoxy-4-nitroaniline as a diazo component and 2-methoxyacetoacetoanilide as a coupling component has advantages of excellent light resistance and clearness but has disadvantages of extremely poor transparency and color strength.

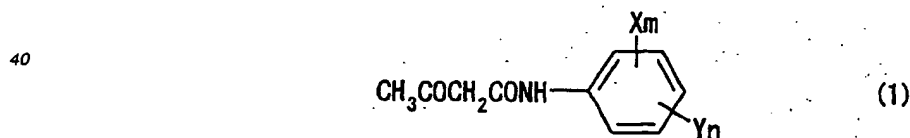
- 20 [0004] For improving the transparency and color strength of the pigment yellow 74, a surface-treatment technique is conventionally adopted. This technique is a method in which a rosin alkali salt solution (so-called rosin soap) is added into a coupler component or into a pigment slurry after coupling and then a metal salt for a lake such as aluminium sulfate is added to deposit the rosin, as an insoluble rosin lake metal salt, on a pigment surface, whereby a pigment particle shape is finely controlled. However, this technique is not sufficient.

- 25 [0005] Under the present situation, for the above reason, the pigment yellow 74 is only partially used for a building material coating composition, etc., which is required to have hiding power, and its applications to a printing ink which is required to have higher transparency and color strength have been hardly developed.

## Summary of the Invention

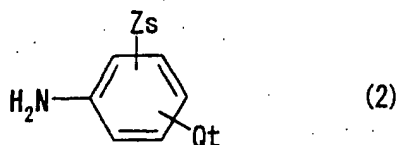
- 30 [0006] It is an object of the present invention to provide a pigment yellow 74 which is improved in transparency and color strength without impairing its inherent light resistance and clearness.

- 35 [0007] According to the present invention, there is provided a pigment yellow 74 obtained by coupling a coupler component containing 2-methoxyacetoacetoanilide and an acetoacetoanilide derivative of the following formula (1) in an amount of 0.1 to 10 mol %, based on the 2-methoxyacetoacetoanilide, and a diazo component obtained by diazotizing 2-methoxy-4-nitroaniline,



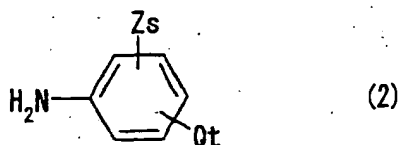
- 45 wherein X may be the same or different and is  $\text{CONR}_1\text{R}_2$ ,  $\text{SO}_2\text{NR}_1\text{R}_2$ ,  $\text{NHCOR}_1$ ,  $\text{CONH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$  or  $\text{SO}_2\text{NH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$  (in which each of  $\text{R}_1$  and  $\text{R}_2$  is independently a hydrogen atom or an alkyl group, or  $\text{R}_1$  and  $\text{R}_2$  together form a cyclic structure, and  $k$  is an integer of 1 to 4),  $m$  is 1 or 2,  $Y$  may be the same or different and is  $\text{R}_3$ ,  $\text{OR}_3$  (in which  $\text{R}_3$  is a hydrogen atom or an alkyl group),  $\text{COOH}$  or  $\text{SO}_3\text{H}$ , and  $n$  is an integer of 0 to 2.

- 50 [0008] According to the present invention, further, there is provided a pigment yellow 74 according to the above, wherein the diazo component is obtained by diazotizing the 2-methoxy-4-nitroaniline and an aniline derivative of the following formula (2) in an amount of 0.1 to 10 mol % based on the 2-methoxy-4-nitroaniline,



10 in which Z may be the same or different and is  $\text{CONR}_1\text{R}_2$ ,  $\text{SO}_2\text{NR}_1\text{R}_2$ ,  $\text{CONH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$ ,  $\text{SO}_2\text{NH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$ ,  $\text{COOH}$  or  $\text{SO}_3\text{H}$  (in which each of  $\text{R}_1$  and  $\text{R}_2$  is independently a hydrogen atom or an alkyl group, or  $\text{R}_1$  and  $\text{R}_2$  together form a cyclic structure, and  $k$  is an integer of 1 to 4),  $s$  is an integer of 1 or 2,  $\text{Q}$  may be the same or different and is  $\text{R}_3$ ,  $\text{OR}_3$  or  $\text{NO}_2$  (in which  $\text{R}_3$  is a hydrogen atom or an alkyl group), and  $t$  is an integer of 0 to 2.

15 [0009] According to the present invention, further, there is provided a pigment yellow 74 obtained by coupling a coupler component containing 2-methoxyacetoacetoanilide with a diazo component obtained by diazotizing 2-methoxy-4-nitroaniline and an aniline derivative of the formula (2) in an amount of 0.1 to 10 mol % based on the 2-methoxy-4-nitroaniline,



wherein Z may be the same or different and is  $\text{CONR}_1\text{R}_2$ ,  $\text{SO}_2\text{NR}_1\text{R}_2$ ,  $\text{CONH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$ ,  $\text{SO}_2\text{NH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$ ,  $\text{COOH}$  or  $\text{SO}_3\text{H}$  (in which each of  $\text{R}_1$  and  $\text{R}_2$  is independently a hydrogen atom or an alkyl group, or  $\text{R}_1$  and  $\text{R}_2$  together form a cyclic structure, and  $k$  is an integer of 1 to 4),  $s$  is an integer of 1 or 2,  $\text{Q}$  may be the same or different and is  $\text{R}_3$ ,  $\text{OR}_3$  or  $\text{NO}_2$  (in which  $\text{R}_3$  is a hydrogen atom or an alkyl group), and  $t$  is an integer of 0 to 2.

30 [0010] According to the present invention, further, there is provided a printing ink composition comprising the pigment yellow 74 recited the above and a vehicle for a printing ink.

#### Detailed Description of the Invention

35 [0011] In the present invention,  $\text{R}_1$  and  $\text{R}_2$  in an acetoacetoanilide derivative of the formula (1) and an aniline derivative of the formula (2) are each a hydrogen atom or an alkyl group. As the alkyl group, preferred is an alkyl group having 1 to 18 carbon atoms, and an alkyl group having 1 to 4 carbon atoms is more preferred. Further, as a cyclic structure obtained by bonding of  $\text{R}_1$  and  $\text{R}_2$ , there is a five-membered ring or a six-membered ring. The above cyclic structure may further contain a nitrogen atom or an oxygen atom as a constituent component.

40 [0012] Examples of an amine residue represented by  $\text{-NR}_1\text{R}_2$  in the formula (1) and the formula (2) include a methylamino group, an ethylamino group, a stearyl amino group, a dimethylamino group, a diethylamino group, a methylaminopropylamino group, a dimethylaminopropylamino group, a diethylaminopropylamino group and a N-aminoethyl-4-pipecolinyl group, while the amine residue shall not be limited to these examples.

45 [0013] Further,  $\text{R}_3$  in the formula (1) is a hydrogen atom or an alkyl group. As the alkyl group, an alkyl group having 1 to 4 carbon atoms is preferred.

[0014] Further, examples of an aniline derivative having a carboxyl group or a sulfonic group include 4-methoxyaniline-2-sulfonic acid, 2,5-dimethoxyaniline-4-sulfonic acid, 2-nitroaniline-4-sulfonic acid and 2-chloro-4-sulfo-5-aminobenzoic acid.

50 [0015] The pigment yellow 74 of the present invention can be produced according to a conventionally-known method. That is, 2-methoxy-4-nitroaniline is diazotized to prepare a diazonium component, on the other hand, the acetoacetoaniline derivative of the formula (1) in an amount of 0.1 to 10 mol %, preferably 1 to 5 mol %, based on 2-methoxyacetoacetoanilide, is added to 2-methoxyacetoacetoanilide to prepare a coupling component, and the diazonium component and the coupling component are coupled according to a general method.

55 [0016] Further, when the aniline derivative of the formula (2) is used as a diazo component, the aniline derivative in an amount of 0.1 to 10 mol %, preferably 1 to 5 mol %, based on 2-methoxy-4-nitroaniline, is added to 2-methoxy-4-nitroaniline, then the resultant mixture is diazotized and coupling is similarly carried out. The coupling reaction is not specially limited, and it may be a batch method carried out under an acidic condition of acetic acid, which is usually

called an acid dipping method, or a continuous method in which a diazo solution and a coupling solution are simultaneously added in equal reaction amounts.

[0017] The pigment yellow 74 of the present invention in the state of a wet cake is flushed with a vehicle for a printing ink to prepare a printing ink. Otherwise, a powdery pigment of the pigment yellow 74 is kneaded with a vehicle for a printing ink to prepare a printing ink. The pigment for the flushing can be obtained as a wet cake by filtrating and washing a slurry after coupling and compressing it such that a pigment content becomes 26 to 32 % by weight. The powdery pigment can be obtained by drying the wet cake and pulverizing the dried wet cake.

[0018] When an offset printing ink is produced by using the pigment yellow 74 of the present invention, flushing is carried out with a flusher and, in this case, 180 to 220 parts by weight of an offset printing ink vehicle is added to 100 parts by weight of the wet cake as a dry pigment. The preparation of an ink from the powdery pigment is carried out with a three-roll mill and, in this case, 350 to 450 parts by weight of a vehicle for an offset printing ink is added to 100 parts by weight of the powdery pigment.

[0019] The pigment yellow 74 of the present invention can be used as a yellow pigment for an offset printing ink for process ink. An offset printing ink composition is composed of 3 to 35 % by weight of the pigment yellow 74 of the present invention, 97 to 45 % by weight of a vehicle for an offset printing ink and 0 to 20 % by weight of other auxiliary agents (a dryer, a leveling-improving agent or a thickening agent) or an extender pigment. The vehicle for an offset printing ink is generally composed of 20 to 50 % by weight of a resin, 0 to 30 % by weight of a vegetable oil and 10 to 60 % by weight of a solvent. Examples of the resin include a rosin-modified phenol resin, a petroleum resin, an alkyd resin or drying-oil-modified resins of these. Examples of the vegetable oil include linseed oil, tung oil and soybean oil. Examples of the solvent include n-paraffin, isoparaffin, aromatic, naphthene and  $\alpha$ -olefin. Further, various known additives for an ink, such as a dryer or a leveling-improving agent, are incorporated to prepare the printing ink composition.

[0020] The pigment yellow 74 of the present invention can be used as a yellow pigment for a gravure printing ink for a process ink. A vehicle for a gravure printing ink is generally composed of 10 to 50 % by weight of a resin and 30 to 80 % by weight of a solvent. Examples of the resin include a gum rosin, a wood rosin, a tall oil rosin, a lime rosin, a rosin ester, a maleic resin, a polyamide resin, a vinyl resin, cellulose nitrate, cellulose acetate, ethyl cellulose, chlorinated rubber, cyclized rubber, an ethylene-vinyl acetate copolymer resin, a polyurethane resin, a polyester resin, an alkyd resin, an acrylic resin, gilsonite, dammar, shellac, mixtures of these, water-soluble resins obtained by rendering any one of the above resins or a mixture of these water-soluble, or an emulsion resin. Examples of the solvent include hydrocarbon, alcohol, ketone, ether alcohol, ether, ester and water.

[0021] The pigment yellow 74 of the present invention can be used as a yellow pigment for a color-electrophotographic toner, for water-based and oil-based inkjet recording liquids, and for a resist ink which is used for a color filter for a liquid crystal display and contains a photosensitive resin as a main component.

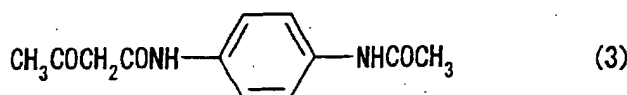
#### Effect of the Invention

[0022] According to the present invention, there is provided a pigment yellow 74 which is improved in transparency and color strength without impairing its inherent light resistance and clearness.

[0023] The present invention will be explained with reference to Examples in detail hereinafter, in which "part" stands for "part by weight" and "%" stands for "% by weight" unless otherwise specified.

#### Example 1

[0024] 168 parts of 2-methoxy-4-nitroaniline was dissolved in a solvent containing 2,000 parts of water and 260 parts of 35 % hydrochloric acid to obtain a solution, and 1,000 parts of ice was added to the solution to cool it to 0 °C. A solution containing 200 parts of water and 70 parts of sodium nitrite was added to the cooled solution, and the resultant mixture was stirred at 3 °C or lower for 60 minutes, to obtain a diazo component. On the other hand, 200 parts of 2-methoxyacetoacetanilide and 8 parts of a compound of the following formula (3) were dissolved in a solution containing 5,000 parts of water and 100 parts of sodium hydroxide. 200 parts of 80 % acetic acid was gradually added to the resultant solution to prepare a suspension as a coupler component. The diazo component was added to the coupler component over 60 minutes, to obtain a pigment slurry. The reaction temperature was kept at approximately 20 °C. The pH of the pigment slurry was adjusted to 9.5 to 10.0 with sodium hydroxide, and then 70 parts of a 25 % rosin soap was added to the slurry. The resultant slurry was stirred for 10 minutes and then hydrochloric acid was added to adjust its pH to 5.0 and to deposit the rosin on a pigment surface. Then, filtration, washing with water and compressing were carried out to obtain a wet cake having a pigment content of 27.5 %. Further, part of the wet cake was dried and pulverized to obtain a pigment powder.



5

[0025] An ink was prepared by flushing with a flusher having a volume of 1 liter. In this preparation, 100 parts, as a dry weight, of the above wet cake and 190 parts of an ink vehicle for offset which had been heated up to 100°C were simultaneously poured into the flusher and flushing was carried out. Then, water generated by the flushing was removed and then heating was carried out for 30 minutes under a reduced pressure ( $1 \sim 8 \times 10^3$  Pa) until the internal temperature of a kneaded mixture reached to 100 °C, thereby completely removing water of the kneaded mixture. 280 parts of an ink vehicle for offset and 50 parts of a solvent were gradually added to the kneaded mixture and then the resultant mixture was taken out from the flusher. Then, the mixture was kneaded with a three-roll mill at a roll temperature of 60 °C under a pressure of 10 Barr, and coarse particles were removed to obtain a base ink. 25 parts of an ink vehicle for offset, 10 parts of a solvent and 3 parts of an auxiliary agent were added to 62 parts of the base ink to adjust tackiness to 5.8 to 6.0, whereby an ink as an end product was obtained.

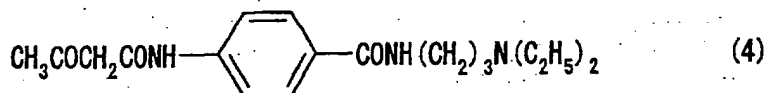
[0026] In the case of the pigment powder, 100 parts of the pigment was added to 400 parts of an ink vehicle for offset and dispersing was carried out using a three-roll mill to obtain a base ink. An ink vehicle for offset, a solvent and an auxiliary agent were added to the base ink to adjust tackiness to 5.8 to 6.0, whereby an ink as an end product was obtained.

#### Example 2

[0027] A wet cake having a pigment content of 27.0 % and a pigment powder were obtained in the same manners as in Example 1 except that 168 parts of 2-methoxy-4-nitroaniline was used to prepare a diazo component and that 200 parts of 2-methoxyacetoacetoanilide and 11 parts of a compound of the following formula (4) were used to prepare a coupler component.

[0028] Inks as an end product were prepared in the same manners as in Example 1.

30



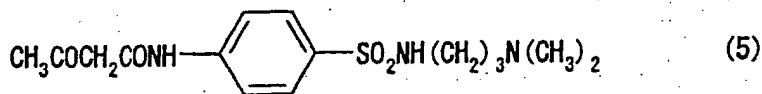
35

#### Example 3

[0029] A wet cake having a pigment content of 27.5 % and a pigment powder were obtained in the same manners as in Example 1 except that 168 parts of 2-methoxy-4-nitroaniline was used to prepare a diazo component and that 200 parts of 2-methoxyacetoacetoanilide and 11 parts of a compound of the following formula (5) were used to prepare a coupler component.

[0030] Inks as an end product were prepared in the same manners as in Example 1.

45



50

#### Example 4

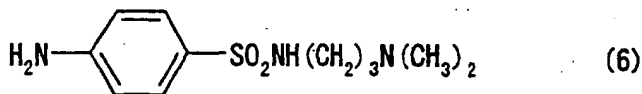
[0031] A wet cake having a pigment content of 27.0 % and a pigment powder were obtained in the same manners as in Example 1 except that 165 parts of 2-methoxy-4-nitroaniline and 4 parts of 2-nitroaniline-4-sulfonic acid were used to prepare a diazo component and that 200 parts of 2-methoxyacetoacetoanilide and 11 parts of a compound of the above formula (5) were used to prepare a coupler component.

[0032] Inks as an end product were prepared in the same manners as in Example 1.

## Example 5

[0033] A wet cake having a pigment content of 27.0 % and a pigment powder were obtained in the same manners as in Example 1 except that 164 parts of 2-methoxy-4-nitroaniline and 9 parts of a compound of the following formula (6) were used to prepare a diazo component and that 200 parts of 2-methoxyacetoacetoanilide and 11 parts of a compound of the above formula (5) were used to prepare a coupler component.

[0034] Inks as an end product were prepared in the same manners as in Example 1.



## Example 6

[0035] 165 parts of 2-methoxy-4-nitroaniline and 4 parts of 2-nitroaniline-4-sulfonic acid were dissolved in a solution containing 2,000 parts of water and 260 parts of 35 % hydrochloric acid to obtain a solution, and 1,000 parts of ice was added to the solution to cool it to 0 °C. A solution containing 200 parts of water and 70 parts of sodium nitrite was added to the cooled solution and the resultant mixture was stirred at 3 °C or lower for 60 minutes, to obtain a diazo component. On the other hand, 207 parts of 2-methoxyacetoacetoanilide was dissolved in a solution containing 5,000 parts of water and 100 parts of sodium hydroxide. 200 parts of 80 % acetic acid was gradually added to the resultant solution to prepare a suspension as a coupler component. The diazo component was added to the coupler component over 60 minutes, to obtain a pigment slurry. The reaction temperature was kept at approximately 20 °C. The pH of the pigment slurry was adjusted to 9.5 to 10.0 with sodium hydroxide, and then 70 parts of a 25 % rosin soap was added to the slurry. The resultant slurry was stirred for 10 minutes and then hydrochloric acid was added to adjust its pH to 5.0 and to deposit the rosin on a pigment surface. Then, filtration, washing with water and compressing were carried out to obtain a wet cake having a pigment content of 27.5 %. Further, part of the wet cake was dried and pulverized to obtain a pigment powder.

[0036] Inks as an end product were prepared in the same manners as in Example 1.

## Example 7

[0037] A wet cake having a pigment content of 27.0 % and a pigment powder were obtained in the same manners as in Example 6 except that 164 parts of 2-methoxy-4-nitroaniline and 9 parts of a compound of the above formula (6) were used to prepare a diazo component and that 207 parts of 2-methoxyacetoacetoanilide was used to prepare a coupler component.

[0038] Inks as an end product were prepared in the same manners as in Example 1.

## Example 8

[0039] A wet cake having a pigment content of 26.7 % and a pigment powder were obtained in the same manners as in Example 6 except that 164 parts of 2-methoxy-4-nitroaniline and 5 parts of 5-aminosalicylic acid were used to prepare a diazo component and that 207 parts of 2-methoxyacetoacetoanilide was used to prepare a coupler component.

[0040] Inks as an end product were prepared in the same manners as in Example 1.

## Comparative Example 1

[0041] A wet cake having a pigment content of 27.3 % and a pigment powder were obtained in the same manners as in Example 1 except that 168 parts of 2-methoxy-4-nitroaniline was used to prepare a diazo component and that 207 parts of 2-methoxyacetoacetoanilide was used to prepare a coupler component.

[0042] Inks as an end product were prepared in the same manners as in Example 1.

[0043] Table 1 shows results from the wet cakes and the pigment powders.

[0044] Transparency: An end product ink was interposed with two transparent film sheets and then a sample was prepared so as to have a thickness of 1 mm. The sample was measured for a L\* value with a color machine and the L\* value was used as an index of transparency. Transparency increases with decreasing the L\* value.

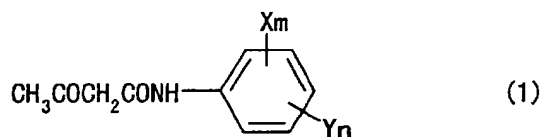
[0045] Color strength: Printing using an end product ink was carried out on a coat paper with a printing machine to form a printing of  $3.0 \times 10^{-2} \text{g/cm}^3$ . Color strength increases with increasing a Gretag value. Color strength was measured with a reflectivity densitometer.

[0051] Table 1

	Wet cake		Pigment powder	
	Transparency	Color strength	Transparency	Color strength
Example 1	75.7	2.10	78.0	1.57
Example 2	66.3	2.11	76.5	1.69
Example 3	67.1	2.12	76.7	1.72
Example 4	66.8	2.10	75.3	1.74
Example 5	66.3	2.11	75.0	1.76
Example 6	76.1	1.98	77.0	1.68
Example 7	69.6	2.08	77.5	1.72
Example 8	77.5	1.96	78.1	1.65
Comparative Example 1	84.7	1.50	85.1	1.38

# Claims

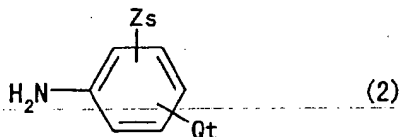
1. A pigment yellow 74 obtainable by coupling a coupler component comprising 2-methoxyacetoacetoanilide and an acetoacetoanilide derivative of formula (1):



wherein each X may be the same or different and is  $\text{CONR}_1\text{R}_2$ ,  $\text{SO}_2\text{NR}_1\text{R}_2$ ,  $\text{NHCOR}_1$ ,  $\text{CONH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$  or  $\text{SO}_2\text{NH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$  (in which each of  $\text{R}_1$  and  $\text{R}_2$  is independently a hydrogen atom or an alkyl group, or  $\text{R}_1$  and  $\text{R}_2$  together form a cyclic structure, and  $k$  is an integer of 1 to 4),  $m$  is 1 or 2, each Y may be the same or different and is  $\text{R}_3$ ,  $\text{OR}_3$  (in which  $\text{R}_3$  is a hydrogen atom or an alkyl group),  $\text{COOH}$  or  $\text{SO}_3\text{H}$ , and  $n$  is an integer of 0 to 2,

in an amount of 0.1 to 10 mol %, based on the 2-methoxyacetoacetoanilide, and a diazo component obtainable by diazotizing 2-methoxy-4-nitroaniline.

2. A pigment yellow 74 according to claim 1, wherein the diazo component is obtainable by diazotizing the 2-methoxy-4-nitroaniline and an aniline derivative of formula (2):

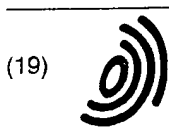


wherein each Z may be the same or different and is  $\text{CONR}_1\text{R}_2$ ,  $\text{SO}_2\text{NR}_1\text{R}_2$ ,  $\text{CONH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$ ,  $\text{SO}_2\text{NH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$ ,  $\text{COOH}$  or  $\text{SO}_3\text{H}$  (in which each of  $\text{R}_1$  and  $\text{R}_2$  is independently a hydrogen atom or an alkyl group, or  $\text{R}_1$  and  $\text{R}_2$  together form a cyclic structure, and  $k$  is an integer of 1 to 4),  $s$  is an integer of 1 or 2, each Q may

be the same or different and is  $R_3$ ,  $OR_3$  or  $NO_2$  (in which  $R_3$  is a hydrogen atom or an alkyl group), and  $t$  is an integer of 0 to 2,  
in an amount of 0.1 to 10 mol % based on the 2-methoxy-4-nitroaniline.

- 5 3. A pigment yellow 74 obtainable by coupling a coupler component comprising 2-methoxyacetoacetoanilide with a diazo component obtainable by diazotizing 2-methoxy-4-nitroaniline and an aniline derivative of formula (2) as defined in claim 2 in an amount of 0.1 to 10 mol % based on the 2-methoxy-4-nitroaniline.
- 10 4. A printing ink composition comprising a pigment yellow 74 according to any one of claims 1 to 3 and a vehicle for a printing ink.
- 15 5. A process for preparing a pigment yellow 74, which process comprises coupling a coupler component comprising 2-methoxyacetoacetoanilide and an acetoacetoanilide derivative of formula (1) as defined in claim 1 in an amount of 0.1 to 10 mol %, based on the 2-methoxyacetoacetoanilide, and a diazo component obtained by diazotizing 2-methoxy-4-nitroaniline.
- 20 6. A process according to claim 5, wherein the diazo component is obtained by diazotizing the 2-methoxy-4-nitroaniline and an aniline derivative of formula (2) as defined in claim 2 in an amount of 0.1 to 10 mol % based on the 2-methoxy-4-nitroaniline.
- 25 7. A process for preparing a pigment yellow 74, which process comprises coupling a coupler component comprising 2-methoxyacetoacetoanilide with a diazo component obtained by diazotizing 2-methoxy-4-nitroaniline and an aniline derivative of formula (2) as defined in claim 2 in an amount of 0.1 to 10 mol % based on the 2-methoxy-4-nitroaniline.





(19)

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 1 316 588 A3**

(12)

**EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:  
05.11.2003 Bulletin 2003/45

(51) Int Cl.7: **C09B 67/22**, C09B 29/33,  
C09D 11/02

(43) Date of publication A2:  
04.06.2003 Bulletin 2003/23

(21) Application number: **02258353.8**

(22) Date of filing: **03.12.2002**

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR**  
**IE IT LI LU MC NL PT SE SI SK TR**  
Designated Extension States:  
**AL LT LV MK RO**

- **Oshiba, Toshio**  
Chuo-ku, Tokyo 104-0031 (JP)
- **Kawashima, Yoshinori**  
Chuo-ku, Tokyo 104-0031 (JP)
- **Shiromaru, Osamu**  
Chuo-ku, Tokyo 104-0031 (JP)

(30) Priority: **03.12.2001 JP 2001368034**  
**03.12.2001 JP 2001368035**

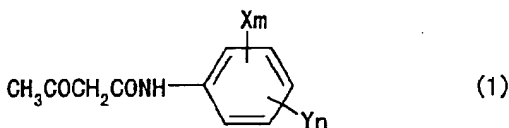
(74) Representative: **Woods, Geoffrey Corlett**  
**J.A. KEMP & CO.**  
Gray's Inn  
14 South Square  
London WC1R 5JJ (GB)

(71) Applicant: **TOYO INK MANUFACTURING CO., LTD.**  
**Tokyo (JP)**

(72) Inventors:  
• **Ishigama, Takayoshi**  
Chuo-ku, Tokyo 104-0031 (JP)

(54) **Pigment yellow 74 and printing ink composition**

(57) A pigment yellow 74 obtainable by coupling a coupler component comprising 2-methoxyacetoacetoanilide and an acetoacetoanilide derivative of formula (1):



wherein each X may be the same or different and is  $\text{CONR}_1\text{R}_2$ ,  $\text{SO}_2\text{NR}_1\text{R}_2$ ,  $\text{NHCOR}_1$ ,  $\text{CONH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$  or  $\text{SO}_2\text{NH}(\text{CH}_2)_k\text{NR}_1\text{R}_2$  (in which each of  $\text{R}_1$  and  $\text{R}_2$  is independently a hydrogen atom or an alkyl group, or  $\text{R}_1$  and  $\text{R}_2$  together form a cyclic structure, and  $k$  is an integer of 1 to 4),  $m$  is 1 or 2, each Y may be the same or different and is  $\text{R}_3$ ,  $\text{OR}_3$  (in which  $\text{R}_3$  is a hydrogen atom or an alkyl group),  $\text{COOH}$  or  $\text{SO}_3\text{H}$ , and  $n$  is an integer of 0 to 2, in an amount of 0.1 to 10 mol %, based on the 2-methoxyacetoacetoanilide, and a diazo component obtainable by diazotizing 2-methoxy-4-nitroaniline; and a printing ink composition comprising the above pigment yellow 74.

**EP 1 316 588 A3**



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 02 25 8353

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 079 303 A (CIBA GEIGY AG) 18 May 1983 (1983-05-18) * claims *	1-7	C09B67/22 C09B29/33 C09D11/02
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 11, 30 September 1998 (1998-09-30) -& JP 10 158555 A (DAINICHISEIKA COLOR & AMP ; CHEM MFG CO LTD), 16 June 1998 (1998-06-16) * abstract *	1-7	
A	EP 1 054 042 A (CIBA SC HOLDING AG) 22 November 2000 (2000-11-22) * claims *	1-7	
A	US 6 261 354 B1 (VERMOORTELE FRANK ET AL) 17 July 2001 (2001-07-17) * claims *	1-7	
A	US 4 496 481 A (WHEELER IAN R) 29 January 1985 (1985-01-29) * claims; examples *	1-7	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	US 4 159 264 A (HAMILTON ALEXANDER ET AL) 26 June 1979 (1979-06-26) * claims *	1,5-7	C09B C09D
A	US 5 024 698 A (SCHWARTZ RUSSELL J ET AL) 18 June 1991 (1991-06-18) * claims *	1,4,5	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15 September 2003	Examiner Serbetsoglou, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03/02 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 02 25 8353

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-09-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0079303	A	18-05-1983	CA 1184704 A1	02-04-1985
			DE 3269679 D1	10-04-1986
			DK 481382 A ,B,	01-05-1983
			EP 0079303 A2	18-05-1983
			JP 1728500 C	19-01-1993
			JP 4012306 B	04-03-1992
			JP 58084873 A	21-05-1983
			US 4457783 A	03-07-1984
JP 10158555	A	16-06-1998	JP 3055673 B2	26-06-2000
EP 1054042	A	22-11-2000	BR 0002478 A	02-01-2001
			CA 2307428 A1	05-11-2000
			EP 1054042 A1	22-11-2000
			JP 2000327943 A	28-11-2000
			US 6361595 B1	26-03-2002
US 6261354	B1	17-07-2001	BE 1011221 A3	01-06-1999
			AU 7327198 A	04-01-1999
			WO 9858026 A1	23-12-1998
			BR 9806749 A	14-03-2000
			EP 0991725 A1	12-04-2000
US 4496481	A	29-01-1985	CA 1202960 A1	08-04-1986
			DE 3174221 D1	30-04-1986
			DK 571181 A ,B,	24-06-1982
			EP 0055218 A2	30-06-1982
			JP 57131256 A	14-08-1982
			KR 8801390 B1	30-07-1988
US 4159264	A	26-06-1979	GB 1547759 A	27-06-1979
			CA 1061334 A1	28-08-1979
			CH 618456 A5	31-07-1980
			DE 2635536 A1	17-02-1977
			FR 2320970 A1	11-03-1977
			IT 1065105 B	25-02-1985
			JP 1266776 C	27-05-1985
			JP 52027433 A	01-03-1977
			JP 59043499 B	22-10-1984
US 5024698	A	18-06-1991	AT 157690 T	15-09-1997
			CA 2078862 A1	23-09-1991
			DE 69127540 D1	09-10-1997
			DE 69127540 T2	22-01-1998
			DK 524941 T3	14-04-1998
			EP 0524941 A1	03-02-1993

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 02 25 8353

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-09-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5024698 A	ES	2107455 T3	01-12-1997
	FI	923865 A	28-08-1992
	JP	5505412 T	12-08-1993
	WO	9114744 A1	03-10-1991
-----			